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Mathematical Techniques for X-Ray Analyzers

North Carolina State Univ. at Raleigh

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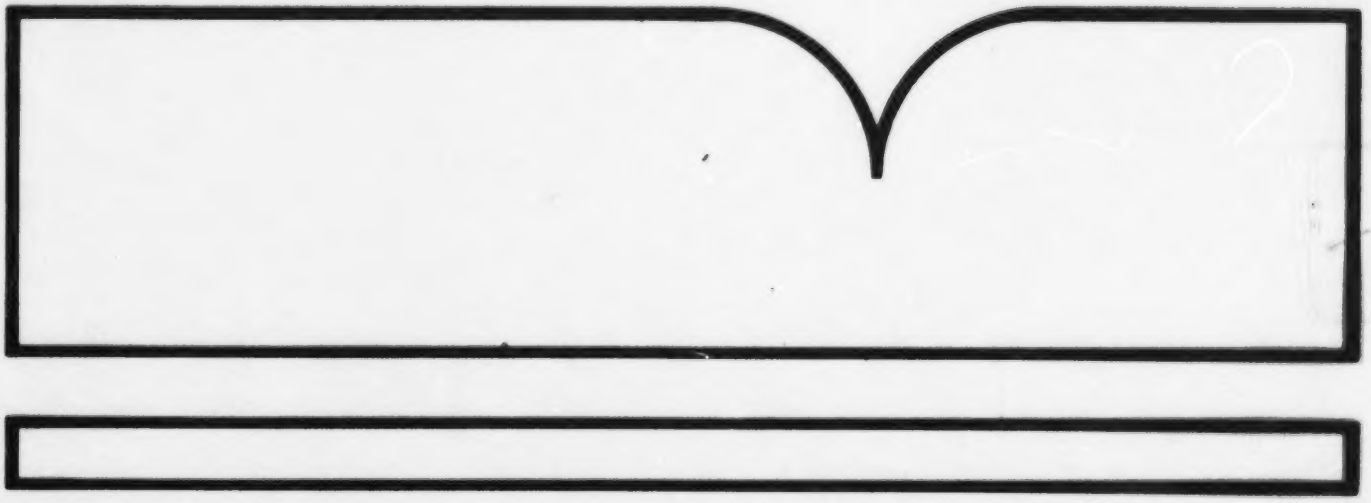

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Mathematical Techniques for X-ray Analyzers

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16. ABSTRACT

Mathematical techniques and subsequent computer software were developed to process energy-dispersive x-ray fluorescence spectra for elemental analysis of airborne particulate matter collected on filters.

The research concerned two areas: (1) determination of characteristic x-ray intensities and (2) determination of elemental amounts from the known characteristic x-ray intensities. In the first area, efforts primarily concentrated on developing and implementating of the library, linear least-squares method and included the two common non-linear aspects of XRF pulse-height spectra: excitation source background and pulse pile up. A detector response function model was also developed for Si(Li) detectors to alleviate the necessity for obtaining and storing extensive complete library spectra for every element of interest. This approach gives improved accuracy, greatly reduces the experimental effort required, and is capable of accounting for variations in detector calibration and resolution without requiring extensive additional experimental effort.

In the second research area the fundamental parameters method was developed by by Monte Carol simulation. Data were collected for several shapes of particles deposited on filters. Empirical correction factors for various practical cases of interest based on these simulations are reported.

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MATHEMATICAL TECHNIQUES FOR X-RAY ANALYZERS

by

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ABSTRACT

A research program was initiated with the overall objective of developing mathematical techniques and subsequent computer software to process energy-dispersive X-ray fluorescence spectra for elemental analyses of airborne particulate matter collected on filters. The research concerned two areas: (1) determination of characteristic X-ray intensities and (2) determination of elemental amounts from the known characteristic X-ray intensities. In the first area, efforts primarily concentrated on developing and implementing the library, linear least-squares method and included the two common non-linear aspects of XRF pulse-height spectra: excitation source background and pulse pile up. A detector response function model was also developed for Si(Li) detectors to alleviate the necessity for obtaining and storing the extensive complete library spectra for every element of interest. This approach gave improved accuracy, greatly reduced the experimental effort required, and was capable of accounting for variations in detector calibration and resolution without requiring extensive additional experimental effort.

In the second research area, the fundamental parameters method was developed by Monte Carlo simulation. Data were collected for several shapes of particles deposited on filters. Empirical correction factors for various practical cases of interest based on these simulations are reported. In addition some more general Monte Carlo simulations were performed for a number of cases. The conditions treated included monoenergetic photon (radioisotope) exciting sources; continuous (X-ray machine) photon exciting sources; homogeneous samples of arbitrary thickness; primary, secondary, and tertiary fluorescence in multi-component samples; and the inclusion of source and characteristic radiation scattering effects.

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SECTION 1

INTRODUCTION

Energy-dispersive X-ray fluorescence (EDXRF) has only been recently developed as a tool for elemental analysis. The use of this principle has probably become of interest largely due to the advent of the high resolution Si(Li) detectors. Combining these detectors with modern multichannel analyzers allows one to accumulate characteristic X-ray pulse-height spectra of many elements simultaneously that are resolved from one another. Therefore, the X-ray analyst interested in EDXRF analysis must be concerned with computational procedures for determining characteristic X-ray intensities for pulse-height energy spectra.

A technique that was developed some time ago for the determination of radioisotope amounts in mixtures from their gamma-ray pulse-height spectra is the library least-squares method (1,2). The primary difference between the radioisotope gamma-ray application and the photon-excited, energy-dispersive X-ray fluorescence intensity application is that the presence of the exciting source in the X-ray fluorescence case gives rise to spectral features that do not obey the basic library linear least-squares assumption. This basic assumption is that the unknown spectrum is a linear combination of all the individual or pure library spectra for the elements involved. This difference was first addressed by Trombka and Schmadebeck (3) for the X-ray fluorescence analysis of thick, homogeneous samples that might be encountered in space exploration studies. In the present work (4,5) it is addressed for the X-ray fluorescence analysis of airborne particulates collected on filters and the library least-squares method is developed and demonstrated for this case.

One of the major problems associated with any type of X-ray fluorescence analysis is that one must often account for sample matrix effects. The intensity of the characteristic X-ray from a given element is a function of all the other elements in the sample matrix through the combined phenomena of enhancement and absorption. The present research addressed this problem specifically for airborne particulates collected on filters (6,7) and for more general cases such as for homogeneous and heterogeneous samples.

Since most of the work described here has been published in the open literature, the present report has been shortened by eliminating the details that can be found there. All of the published work that has been either entirely or partially supported by this grant is listed in the Appendix.

SECTION 2

CONCLUSIONS

Two major mathematical methods have been developed and tested for the EDXRF analysis of airborne particulates collected on filters: (1) the library least-squares analysis of characteristic X-ray pulse-height spectra for determining pure element intensities and (2) the Monte Carlo simulation of characteristic X-ray intensities from particulates of various sizes, shape factors, and compositions for determining elemental amounts from characteristic X-ray intensities. As a result of this work the library least-squares analysis method is now being routinely used by the Environmental Sciences Research Laboratory in the analysis of about 10,000 samples per year.

In addition to these two major mathematical methods, other models have been developed that are useful for certain analysis conditions. In the determination of characteristic X-ray intensities these include: (1) Monte Carlo simulation of the sample scattered exciting photon radiation, (2) a model and method for accounting for pulse pile up, and (3) a model for simulating pure element characteristic X-ray pulse-height spectra based on a model for the Si(Li) response function. In the simulation of characteristic X-ray intensities from known elemental compositions these include: (1) Monte Carlo simulation of discrete photon energy radioisotope exciting sources for homogeneous samples, (2) Monte Carlo simulation of continous and discrete energy X-ray machine exciting sources for homogeneous samples, and (3) the development of a simple semi-empirical model for the prediction of X-ray intensities from particulate and heterogeneous samples that are simply characterized.

SECTION 3

RECOMMENDATIONS

It is recommended that the library least-squares method based on the simple model of the pure element library spectra obtained via the model of the Si(Li) response function be implemented for the determination of characteristic X-ray intensities for the EDXRF analysis of airborne particulates collected on filters.

It is also recommended that matrix correction factors be generated by Monte Carlo simulation for cases of general interest that can be identified for the same application. The methods and subsequent computer programs have been developed and are available to accomplish these tasks.

Additional work is required to delineate the fundamental processes that govern the Si(Li) response function and obtain a more fundamental model for it.

SECTION 4

DETERMINATION OF X-RAY INTENSITIES

The library least-squares method for the determination of characteristic X-ray pulse-height intensities has been developed for photon excitation of airborne particulates collected on filters (4,5). In this case the exciting source radiation is scattered almost entirely by the filter and can be considered to have a constant shape. Different filter thicknesses can be assumed to only alter the intensity of the exciting source scattered spectrum. Therefore, the exciting source scattered spectrum can be obtained from a clean filter and treated as a separate pure library spectrum. This is shown to be a practical and accurate method of treating the exciting source scattered radiation in the case of airborne particulates on filters. For the more general case where the shape of the exciting source scattered radiation varies with sample composition, Monte Carlo simulation of the scattered portion of the spectrum has been developed and demonstrated for a wide variety of homogeneous samples (8,9).

There are a number of minor problems associated with applying the library least-squares method. These include: (1) statistical counting rate fluctuations, (2) gain shift, (3) zero shift, and (4) missing library spectra. These problems have been studied by simulation techniques. In the first study the first three problems were examined for eight elements excited by a titanium secondary fluorescer XRF system. The results of this study are given in Table 1 and are shown in Figures 1 and 2. It is clear from these results that the effect of even small gain and zero shifts are very dramatic and one must minimize electronic drifts of this type if the method is to yield accurate results.

In a second study the problem of detecting missing library spectra was examined by simulation methods. Spectra for the three elements chromium, manganese, and iron in various relative amounts and for various levels of counting statistics were simulated by appropriate use of the existing library least-squares method with spectra. The results are given in Table 2 and in Figures 3 through 6. From these results one may conclude that: (1) the reduced chi-square value is an accurate indicator that elements have been missed if those elements represent about their equal share of the total spectrum, (2) the predicted standard deviations for each elemental amount are good estimates of the errors involved if the controlling source of error is the statistical fluctuations of the counting rates and the chi-square value is close to unity, and (3) the residuals of the least-squares analysis are a very sensitive visual indicator of missed elements. It would probably be quite easy to develop a quantitative mathematical treatment of the visual indication given by the residuals based on the counting rate differences in adjacent channels. However, a suggested alternative (5) is to first use all available library

spectra in an initial "screening" least-squares analysis. Those library spectra that give negative amounts or amounts smaller than some prescribed value are omitted and the least-squares analysis is performed again.

TABLE 1. RESULTS OF A LIBRARY LEAST-SQUARES ANALYSIS OF A SAMPLE

Element	Amount ($\mu g/cm^2$)	Relative standard deviations (%)		
		Simulation A*	Simulation B*	Simulation C*
Argon	0.434	0.508	0.569	0.512
Aluminum	3.098	6.135	4.476	6.554
Silicon	6.653	1.291	1.239	1.282
Phosphorus	0.028	106.781	11.789	194.391
Sulfur	6.659	1.055	1.525	0.981
Chlorine	0.332	4.989	5.033	4.284
Potassium	1.001	1.070	1.027	1.089
Calcium	1.460	0.657	0.732	0.669
Lead	11.721	10.903	2.648	253.989
Reduced chi-square values:		0.964	75.63	4.75

*Simulations A, B, and C are when errors are due only to statistical counting rate fluctuations, a 1 percent gain shift, and a 0.2 channel zero shift, respectively.

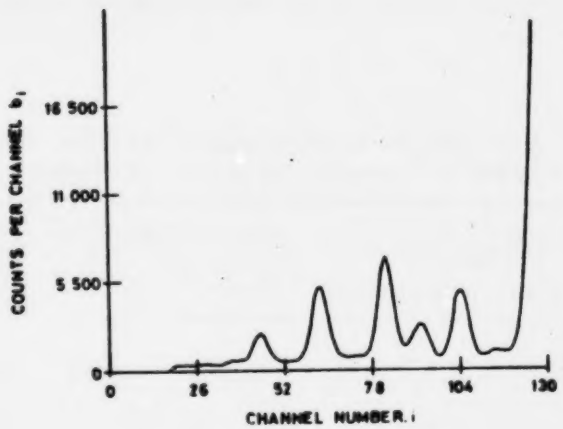

Figure 1. X-ray spectrum containing eight elements excited with a titanium secondary fluorescer XRF system.

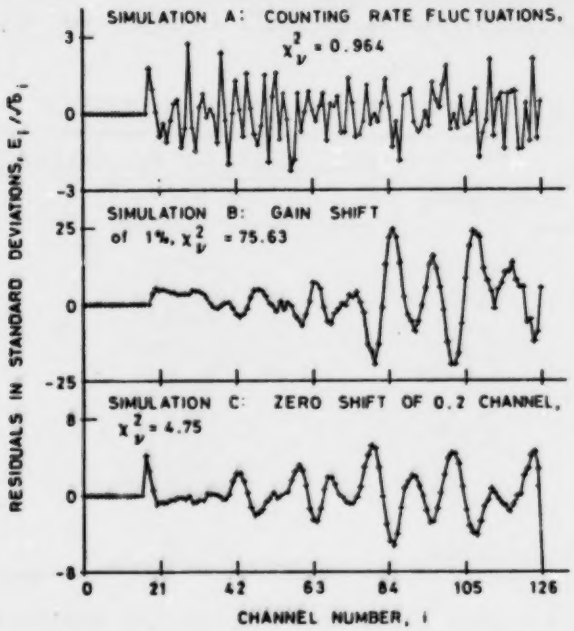

Figure 2. Residuals obtained from the X-ray γ spectrum shown in Figure 1 for various simulated errors after least-squares analysis.

TABLE 2. RESULTS OF A LIBRARY LEAST-SQUARES ANALYSIS FOR TWO SIMULATED PARTICULATE SPECTRA CONTAINING CHROMIUM, MANGANESE, AND IRON

Element	Amounts ($\mu g/cm^2$)		Relative standard deviations (%)			
			Without Mn Library		With Mn Library	
	Case 1 (Good statistics)	Case 2 (Poor statistics)	Case 1	Case 2	Case 1	Case 2
Chromium	13.7	0.274	0.34	2.68	0.36	2.80
Manganese	0.685	0.0274	--	--	3.46	18.93
Iron	13.7	0.274	0.27	2.15	0.28	2.17
Reduced chi-square values:			3.20	1.37	1.10	1.30

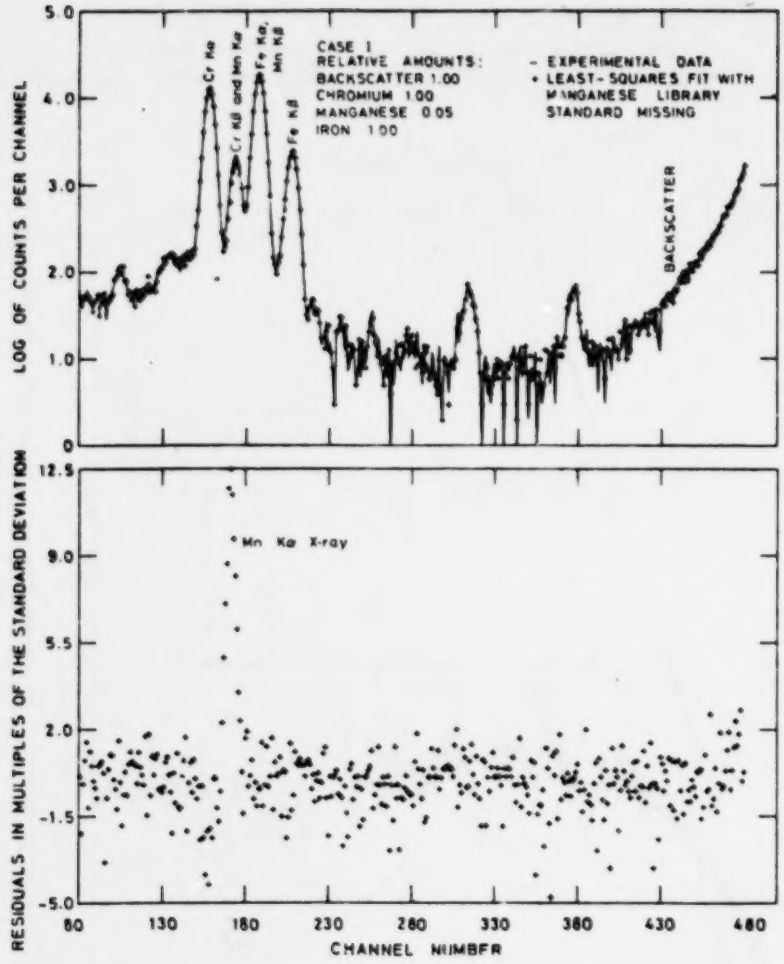

Figure 3. Case 1. Good statistics. X-ray spectra and residuals for relative amounts of backscatter, Cr, Mn, and Fe in the ratios 1.00, 1.00, 0.05, and 1.00 analyzed without the Mn library spectrum.

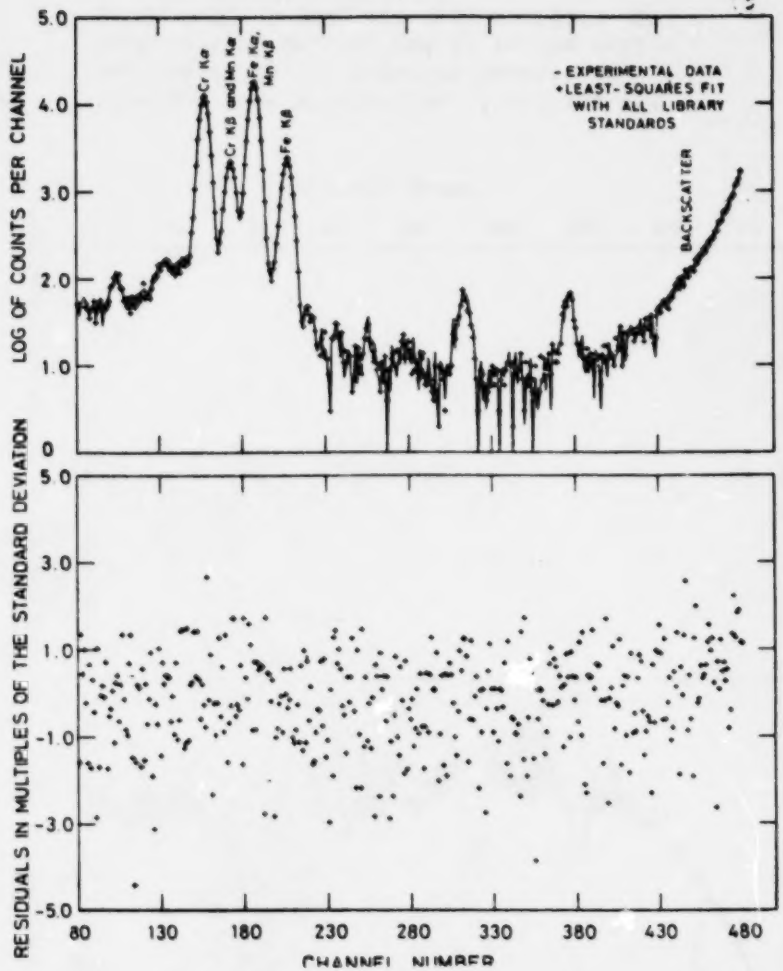

Figure 4. Case 1. Good statistics. X-ray spectra and residuals for relative amounts of backscatter, Cr, Mn, and Fe in the ratios 1.00, 1.00, 0.05, and 1.00 analyzed with the Mn Library included.

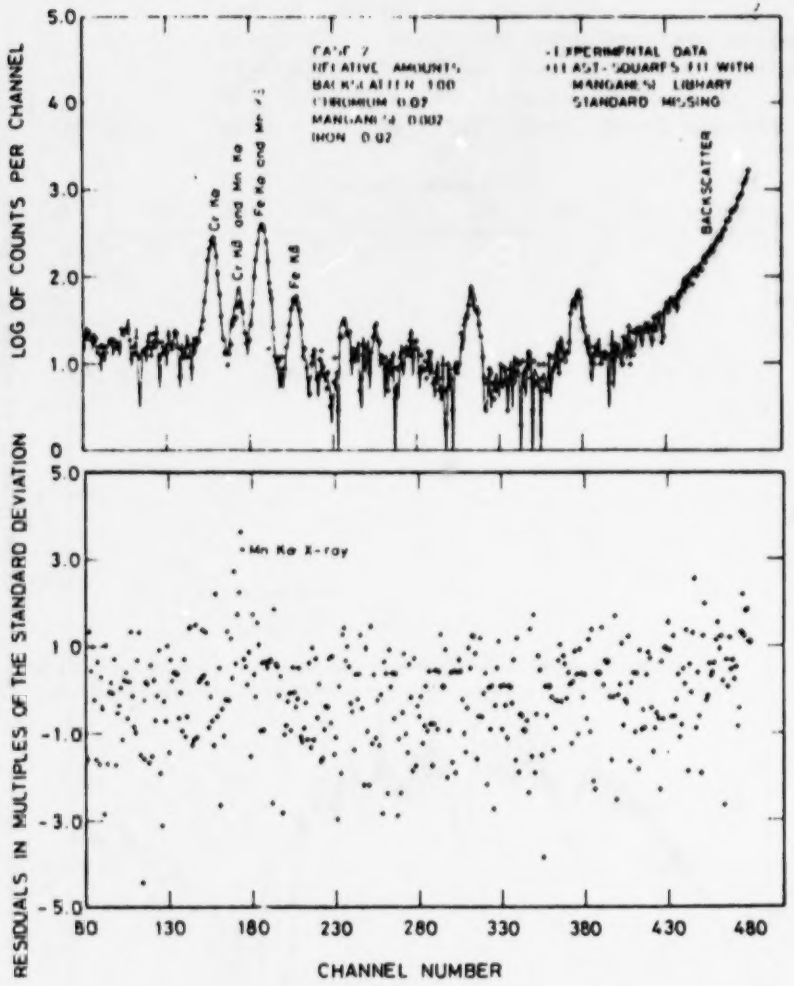

Figure 5. Case 2. Poor statistics. X-ray spectra and residuals for relative amounts of backscatter, Cr, Mn, and Fe in the ratios 1.00, 0.02, 0.002, and 0.02 analyzed without the Mn library spectrum.

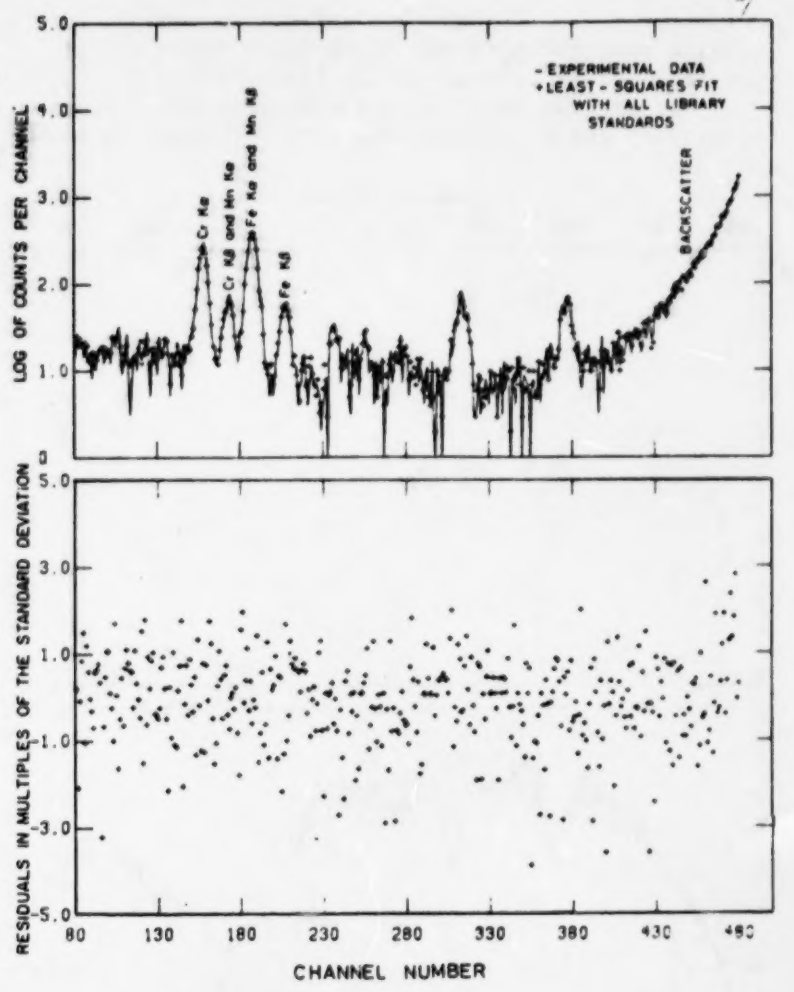

Figure 6. Case 2. Poor statistics. X-ray spectra and residuals for relative amounts of backscatter, Cr, Mn, and Fe in the ratios 1.00, 0.02, 0.002, and 0.02 analyzed with the Mn library included.

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A problem that is encountered in some cases in the application of the library least-squares method is that of the pulse pile-up phenomenon. At high counting rates two (or more) pulses may be analyzed simultaneously giving rise to sum pulses of the wrong magnitude and correspondingly fewer correct individual pulses. This phenomenon can be partially accounted for by the use of electronic pile-up rejection methods. However, it is impossible to eliminate all sum pulses by this method and, therefore, a mathematical model and correction technique has been developed and demonstrated (10,12). It is found that the model and correction technique work quite well and are particularly suited to use with detection systems that include electronic pulse pile-up rejectors.

The model for pulse pile up (10-12) is based on assuming that only two pulses are analyzed simultaneously and that the interval probability distribution applies. To obtain explicit analytical expressions the pulses are assumed to be either parabolic in shape or to be capable of approximation by a low-order polynomial. Results of model predictions based on the parabolic shape and the polynomial approximated pulses are shown in Figure 7. It is obvious that the model is capable of good accuracy in either case, but the polynomial approximated pulses give significnatly better results.

The previously mentioned problem of obtaining the shape of the source backscattered spectrum for the more general problem of homogeneous samples has been studied by using Monte Carlo simulation (8,9). Monte Carlo models were developed that considered the five cases: (1) single Rayleigh (coherent) scattering, (2) single Compton (incoherent) scattering, (3) double Compton scattering, (4) Compton-Rayleigh scattering, and (5) Rayleigh-Compton scattering. A typical set of predicted results are shown in Figure 8 for the last four cases. The single Rayleigh case (and multiple Rayleigh scattering) is trivial since no change in energy occurs and the normal Gaussian-shaped pulse with the resolution imposed by the detector is observed. The spectra from these five cases were then used as library spectra in a least-squares program to fit the experimental spectrum from a ^{109}Cd source. The results of the predicted least-squares fit of the individual library spectra are compared to experimental results in Figure 9. It is clear that this technique is quite accurate and should prove useful for homogeneous samples of known thickness.

Another problem in the application of the library least-squares method is the necessity for preparing samples and obtaining the response from all the pure elements of interest to the analyst to obtain library spectra. This is a tedious and frustrating procedure and has the disadvantages that: (1) a large amount of experimental work is required, (2) a large amount of computer storage is necessary, (3) inaccuracies arise due to impurities in the samples and the analyzer system, and (4) any change in the analyzer system (particularly the detector) requires that the library spectra be accumulated again. To alleviate this problem a model of pure element library spectra has been constructed based on first obtaining a model for the Si(Li) detector response function (13,14). This approach has been demonstrated for two Si(Li) detection systems of varying complexity and for a range of elements from manganese to arsenic for excitation with molybdenum K X rays. All of the disadvantages previously listed are alleviated and, in addition, one has the advantage with this method that ratios of the K-α and K-β X rays need not be fixed. One

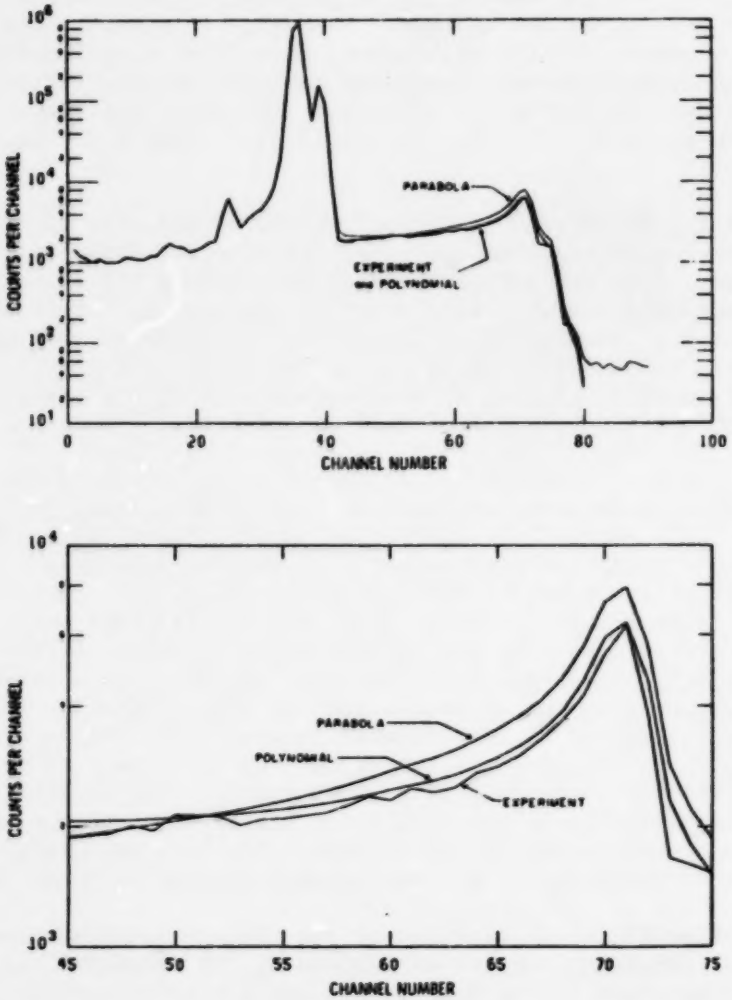

Figure 7. Comparison of an experimental high counting rate spectrum of ^{55}Fe with that predicted by parabolic and polynomial approximated pulse shapes.

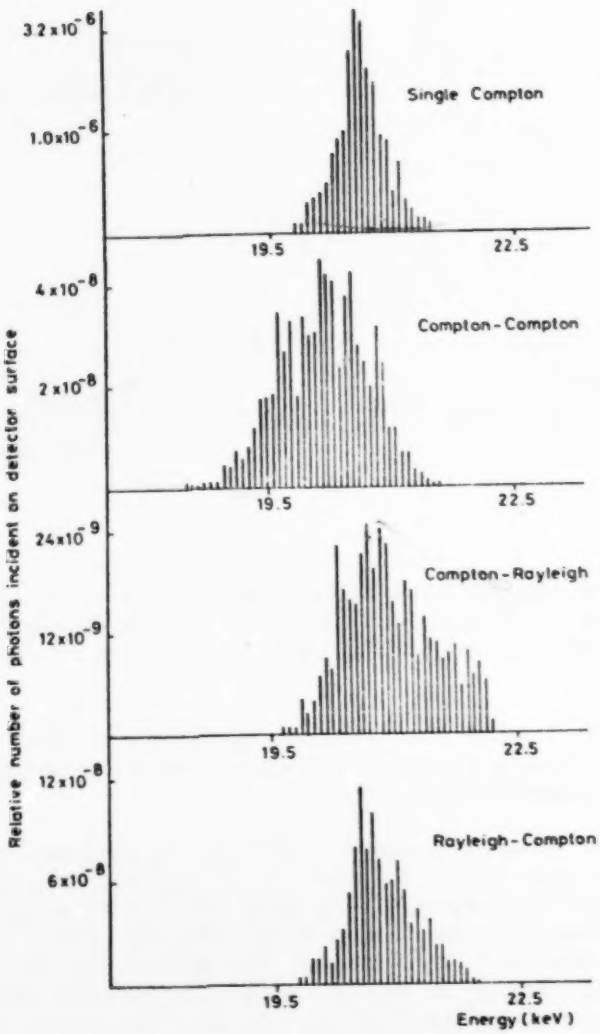

Figure 8. Monte Carlo-predicted photon spectra from the Ag K-α X ray (22.163 keV) scattered from a 5 mm thick Al target.

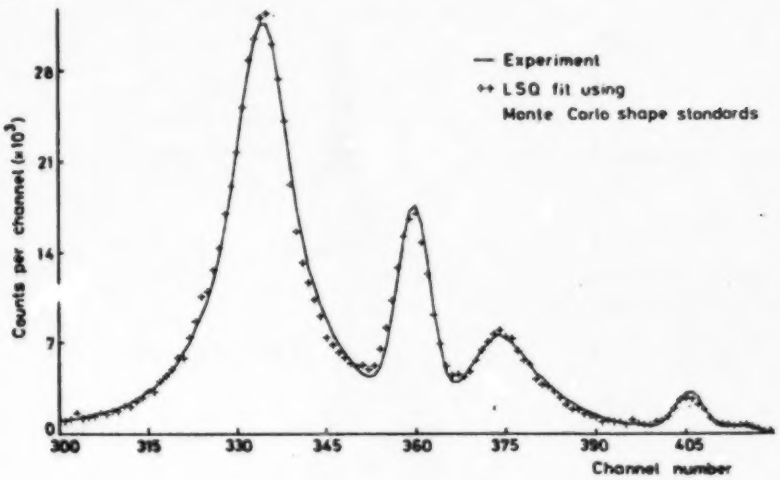

Figure 9. Comparison of the observed backscatter region of the X-ray spectrum from a ^{109}Cd source from a 5mm thick Al sample with that predicted from Monte Carlo-generated shape standards.

only has to have available a few standards containing known amounts of a mixture of elements to utilize the Si(Li) response function model for producing pure element standard libraries.

The Si(Li) response function model for photons up to about 30 keV exhibits five major spectral features. The lowest energy feature results from Compton scattering within the detector. In most cases this occurs at pulse-height energies lower than the lower level discriminator of the spectrometer and, therefore, has no practical importance. The second feature is a flat continuum from the lowest energy up to the center of the main photopeak. The third feature is a truncated exponential tail to the low-energy side of each photopeak. The fourth feature is a Gaussian-shaped silicon X-ray escape peak. The fifth and final feature is the main photopeak which is also Gaussian-Shaped. The last four of these features are illustrated for the two K-α X rays of gallium in Figure 10.

The four parameters required in the response function were obtained for 13 pure element spectra for a double guard-ring Si(Li) detector system. The experimental and model pulse-height spectra for four representative elements are shown in Figures 11 through 14. This data had to be manipulated somewhat since contaminants were present in almost all of the original spectra. In many cases unwanted photopeaks were stripped from the original data. As a result of this some of the model spectra do not correspond to experimental results as well as others. Of the four spectra given two are representative

of the better model fits to experimental data (manganese and gallium) and two are representative of the worse (arsenic and nickel). This points up the fact that the experimental preparation of elemental standards is still a difficult problem. The response function approach should be capable of eliminating this problem by providing consistent, accurate synthetic elemental library spectra.

When an elemental library spectrum is constructed one must also have the relative intensities of each characteristic X ray emitted by that element. These intensities depend upon whether the sample is thin or thick. If desirable one could allow these intensities to be unconstrained and perform a linear least-squares analysis on the intensity of each characteristic X ray separately. The relative intensities actually found for the separate characteristic X rays of a given element gives additional information about the sample being analyzed.

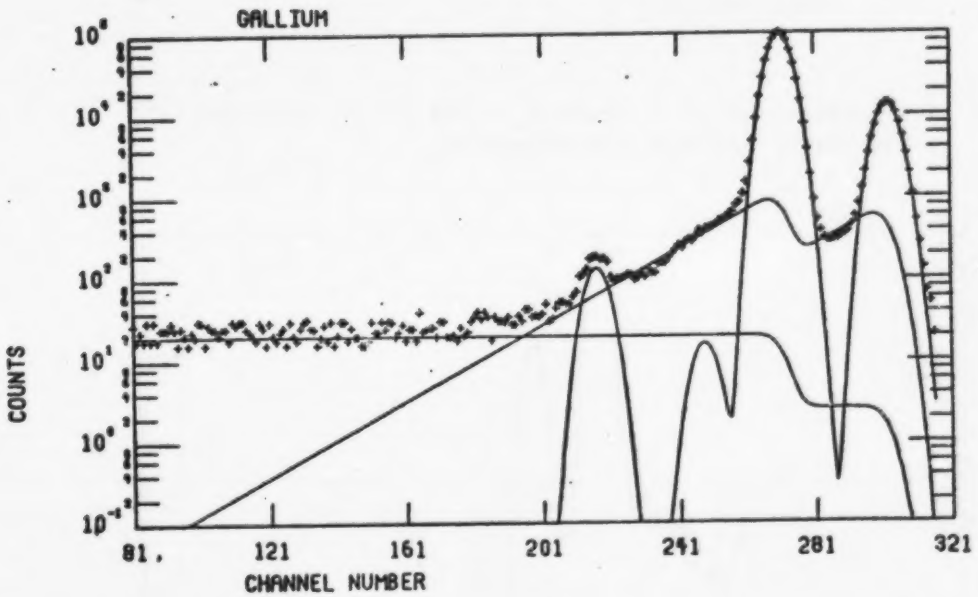

Figure 10. Illustration of the four major spectral features of the two K-α X rays of gallium in a Si(Li) spectrum.

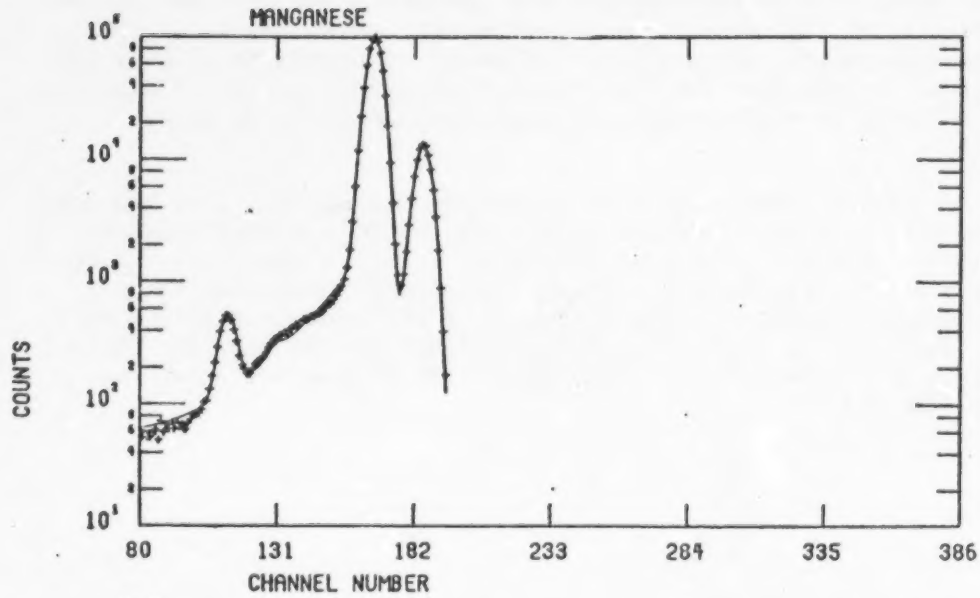

Figure 11. The response function model compared to the experimental pulse-height spectrum for manganese.

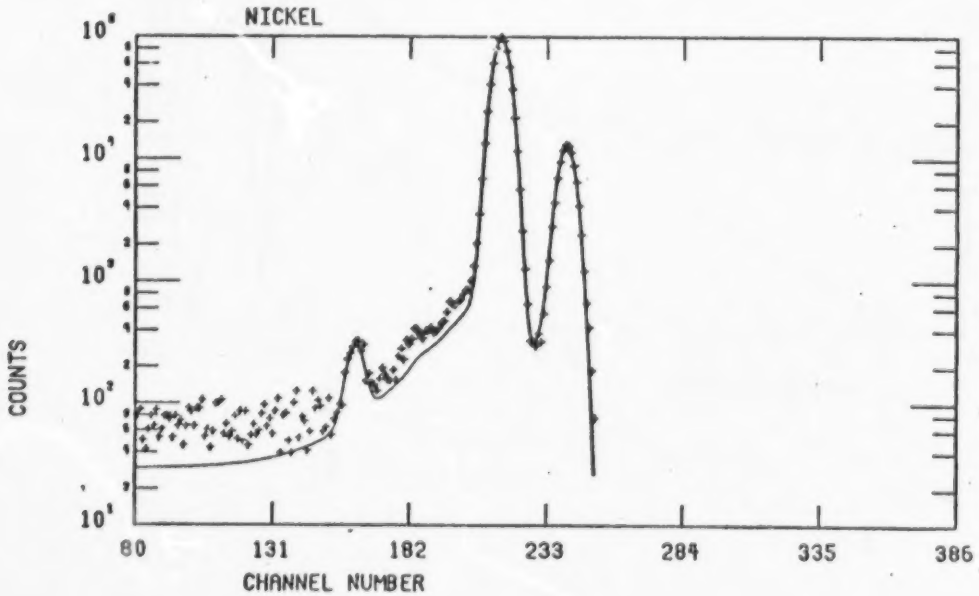

Figure 12. The response function model compared to the experimental pulse-height spectrum with nickel.

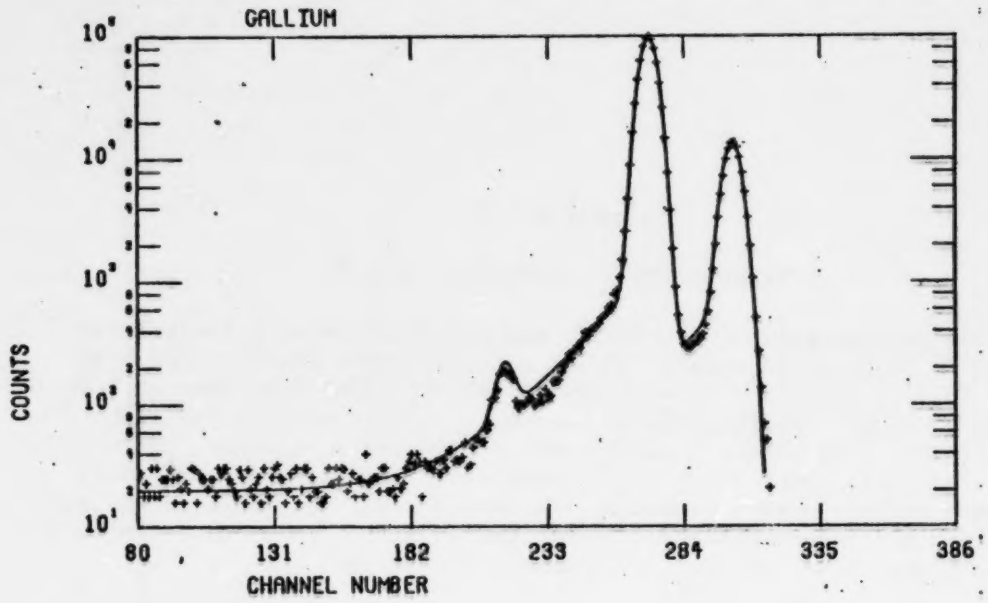

Figure 13. The response function model compared to the experimental pulse-height spectrum for gallium.

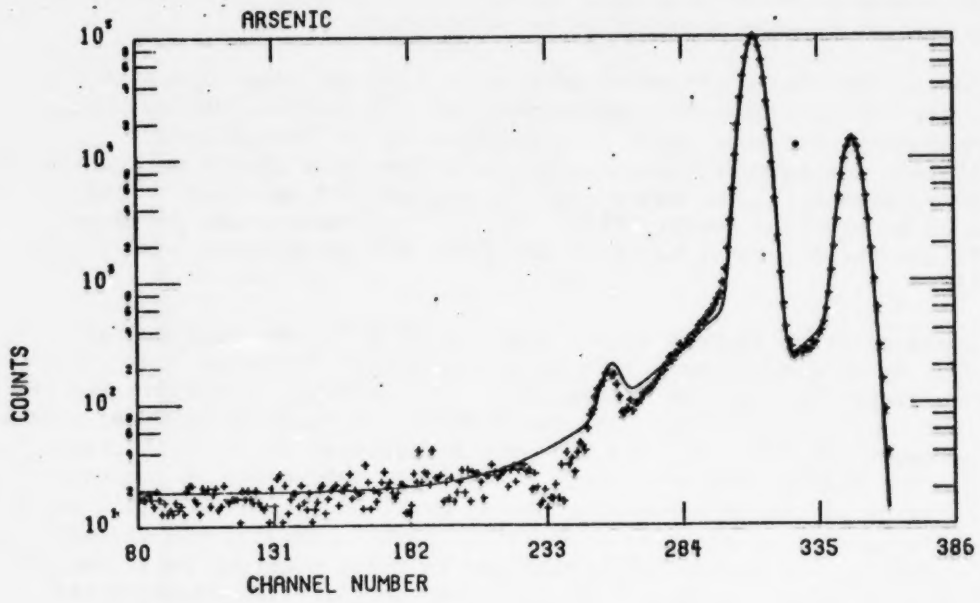

Figure 14. The response function model compared to the experimental pulse-height spectrum for arsenic.

SECTION 5

DETERMINATION OF ELEMENTAL AMOUNTS

For the determination of elemental amounts from characteristic X-ray intensities a Monte Carlo simulation for various sample matrices has been developed (6,7). Results were obtained for particulates deposited on filters excited by photons. Idealized particle shapes such as spheres and right circular cylinders of various lengths were considered. Empirical correction factors for typical cases of practical interest were reported. Secondary fluorescence effects were included in the simulation. This appears to be a useful approach for correcting for sample matrix effects when characteristics of the particulates in the sample are fairly well known.

An example result is shown in Figure 15 for the case of sulfur enhancement by calcium in the form of either CaO, $CaCO_3$, or $CaSO_4 \cdot 2(H_2O)$ as calculated for the idealized cases of uniform spheres or uniform layers. In the case of the CaO and the $CaCO_3$ the sulfur is assumed to be in trace quantities that are uniformly distributed. It is obvious that a significant amount of enhancement occurs in these practical cases of interest and that it must be taken into account if good accuracy is to be obtained.

In addition to this application of primary interest other cases of practical interest have also been treated by Monte Carlo simulation. These include: monoenergetic wide-angle photon excitation of homogeneous samples (15,16), monoenergetic and continuous narrow-beam photon excitation of homogeneous samples (17), and monoenergetic, secondary-fluorescer photon excitation of homogeneous samples (18). Recently a simple model based on Monte Carlo simulated results has been developed for particulate powder samples (19).

The fundamental parameters method consists of using the fundamental parameters of X-ray fluorescence such as photoelectric cross-sections and fluorescence yields in rigorous mathematical relationships for predicting the characteristic X-ray intensities from the elemental amounts in samples. These rigorous mathematical relationships can only be obtained in explicit analytical form for the simple case of a thick homogeneous sample with a constant angle of entrance of the monoenergetic photon exciting source radiation and a constant angle of exit of the characteristic X rays. However, one may obtain primary, secondary, and tertiary fluorescence in these rigorous relationships for this specific case. Primary, secondary, and tertiary fluorescence are defined as the characteristic X rays produced from the element of interest, either directly from the exciting radiation (primary), indirectly through the characteristic X rays from a second element (secondary) or indirectly through the characteristic X rays from a third element, which in turn was produced by the characteristic X rays of a second element (tertiary).

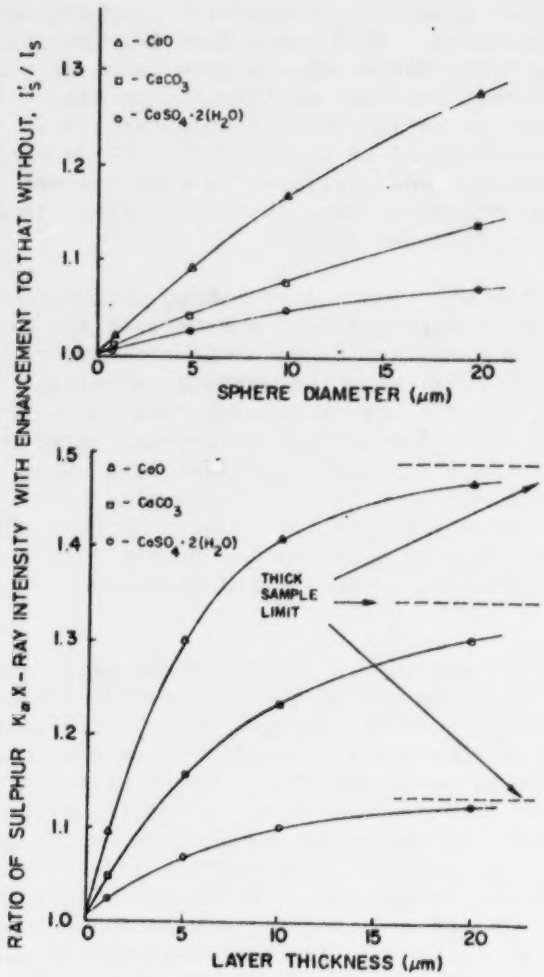

Figure 15. Variation of sulfur enhancement with layer thickness and sphere diameter for various calcium compounds. For CaO and $CaCO_3$ it is assumed that sulfur as a trace element is uniformly dispersed throughout the sphere or layer.

In a series of papers Gardner and Hawthorne (15-18) have extended the fundamental parameters method to a broad range of photon excitation XRF analysis techniques by Monte Carlo simulation. In Ref. 15 a Monte Carlo simulation is derived for a discrete energy exciting source that emits photons isotropically. The analyzer system treated is an annular ring radioisotope source mounted coaxially with a right circular cylindrical homogeneous sample of infinite thickness and a right circular cylindrical detector. This particular problem is fortunately two-dimensional in that symmetry exists about the axis of the circular sample, ring source, and circular detector. This makes the problem much easier to treat than the equivalent three-dimensional problem.

It is possible in treating this problem to accomplish complete variance reduction on the basis of physical principles. This means that the resulting computer program designed to make the Monte Carlo calculations is as efficient as possible and that this is attained without the fear of introducing bias. Typical calculation times for the computer program on an IBM 360/165 computer are 15 seconds to obtain relative standard deviations of 2% or better for three components in one sample when primary, secondary and tertiary fluorescence are considered. The FORTRAN statements for the computer program XRAY designed to accomplish this calculation are available from the authors.

The Monte Carlo simulation was verified by making calculations for an extreme analyzer geometry, which was chosen to approximate the conditions of fixed angle of exciting source entry and fixed angle of characteristic X-ray exit so that the explicit analytical solution derived by Sherman (20,21) is also valid. A comparison of the results obtained by the two methods is given in Table 3. Note that there is no statistical difference between the Monte Carlo results and those from the analytical relationships. Note also that verification of the Monte Carlo simulation with the explicit analytical solution has the advantage over the use of experimental results in that while only the total intensities could be checked by experiment, the explicit analytical solutions provide verification of the primary, secondary and tertiary fluorescence contributions as well.

Reference 17 described the adaptation of this Monte Carlo simulation to the continuous and discrete exciting source photon spectra from conventional X-ray tubes. This is accomplished by obtaining a probability distribution of the X-ray tube exciting source spectrum and sampling from the cumulative distribution constructed from it to begin each Monte Carlo history. The Monte Carlo simulation was verified in this case with the results given by Shiraiwa and Fujino (22,23). They used the analytical relationships for primary, secondary and tertiary fluorescence in homogeneous thick samples for the fixed entrance and exit angles and discrete photon spectra with numerical integration to obtain results for a continuous spectra of exciting photons as would be obtained with a conventional X-ray tube. By using the identical fundamental parameters and form of the X-ray tube spectrum that they used in the Monte Carlo simulation the results are directly comparable. These results are given in Table 4. Note that the average relative error for all results was only 0.95%, while the average Monte Carlo predicted relative standard deviation was 1.47%. This indicates that the Monte Carlo simulation is well within the experimental accuracy attainable with XRF analyses. The computer times required for these calculations were about 45 seconds per case.

Reference 18 describes the extension of the Monte Carlo method to secondary fluorescer X-ray machines. This was accomplished by assuming that a distribution of X-ray intensities from all positions on the secondary fluorescer could be obtained. A simple experimental method for accomplishing this was developed and demonstrated. It consisted of placing a small piece of the fluorescer of interest at known locations on the target and measuring the resulting intensity with a detector located at a fixed distance above the target. The general secondary fluorescer geometry assumed is shown in Figure 16.

TABLE 3. COMPARISON OF INTENSITIES PREDICTED BY THE MONTE CARLO SIMULATION AND THE EXPLICIT ANALYTICAL RELATIONSHIPS

	Sample 1			Sample 2		
Component	Intensity	Error in Monte Carlo prediction (%)	Monte Carlo predicted standard deviation (%)	Intensity	Error in Monte Carlo prediction (%)	Monte Carlo predicted standard deviation (%)
Primary Ni	0.086829	+2.27	2.37	0.59657	-0.31	1.47
Primary Fe	0.33410	+0.03	1.87	0.042168	-0.64	1.66
Primary Cr	0.19167	-1.91	1.65	0.096741	-1.80	1.70
Secondary Ni-Fe	0.023921	+0.75	1.91	0.022259	-0.71	1.96
Secondary Ni-Cr	0.014772	-1.16	1.68	0.052694	-1.70	1.98
Secondary Fe-Cr	0.062348	-0.08	1.79	0.0039275	+1.84	1.92
Tertiary Ni-Fe-Cr	0.0052	-1.92	1.95	0.0026	-7.69	2.49

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TABLE 4. COMPARISON OF RELATIVE INTENSITIES[a] FOR MONTE CARLO AND NUMERICAL CALCULATIONS

Composition (%)	Ni X-rays	Fe X-rays			Cr X-rays				
Ni Fe Cr	Primary	Primary	Secondary	Total	Primary	Secondary-Ni	Secondary-Fe	Tertiary	Total
15 70 15 (Monte Carlo)[b]	0.0651 (2.04%)	0.5277 (1.34%)	0.0220 (1.51%)	0.5497 (1.28%)	0.1525 (1.57%)	0.0042 (1.40%)	0.0473 (1.43%)	0.0023 (1.60%)	0.2063 (1.19%)
(Numerical)[c]	0.064	0.532	0.022	0.558	0.155	0.004	0.047	0.0021	0.208
15 35 50 (Monte Carlo)	0.0694 (2.04%)	0.1753 (1.74%)	0.0068 (1.98%)	0.1821 (1.67%)	0.4788 (1.18%)	0.0164 (1.39%)	0.0527 (1.28%)	0.0027 (1.48%)	0.5506 (1.03%)
(Numerical)	0.069	0.175	0.007	0.182	0.489	0.016	0.052	0.0025	0.559
20 55 25 (Monte Carlo)	0.0914 (1.99%)	0.3614 (1.47%)	0.0201 (1.66%)	0.3815 (1.39%)	0.2458 (1.41%)	0.0101 (1.41%)	0.0530 (1.38%)	0.0036 (1.56%)	0.3124 (1.10%)
(Numerical)	0.090	0.363	0.020	0.383	0.250	0.010	0.052	0.0033	0.315
25 65 10 (Monte Carlo)	0.1152 (1.94%)	0.5279 (1.30%)	0.0396 (1.46%)	0.5675 (1.21%)	0.1018 (1.69%)	0.0048 (1.42%)	0.0312 (1.49%)	0.0027 (1.65%)	0.1404 (1.25%)
(Numerical)	0.114	0.533	0.040	0.573	0.103	0.005	0.031	0.0025	0.141
25 25 50 (Monte Carlo)	0.1246 (1.94%)	0.1253 (1.77%)	0.0086 (2.00%)	0.1339 (1.65%)	0.4733 (1.19%)	0.0288 (1.41%)	0.0369 (1.31%)	0.0033 (1.50%)	0.5422 (1.04%)
(Numerical)	0.123	0.125	0.009	0.134	0.483	0.029	0.037	0.0031	0.552
40 50 10 (Monte Carlo)	0.2064 (1.80%)	0.4061 (1.35%)	0.0539 (1.48%)	0.4600 (1.20%)	0.0097 (1.69%)	0.0085 (1.45%)	0.0035 (1.54%)	0.0035 (1.69%)	0.1350 (1.26%)
	0.205	0.410	0.053	0.463	0.101	0.009	0.023	0.0033	0.135
40 30 30 (Monte Carlo)	0.2155 (1.80%)	0.1859 (1.60%)	0.0234 (1.77%)	0.2093 (1.42%)	0.2853 (1.37%)	0.0278 (1.45%)	0.0316 (1.43%)	0.0048 (1.59%)	0.3495 (1.11%)
(Numerical)	0.213	0.187	0.024	0.210	0.290	0.028	0.031	0.0046	0.354
70 20 10 (Monte Carlo)	0.4766 (1.53%)	0.1659 (1.57%)	0.0497 (1.59%)	0.2156 (1.25%)	0.0972 (1.73%)	0.0191 (1.58%)	0.0091 (1.78%)	0.0031 (1.82%)	0.1235 (1.31%)
(Numerical)	0.478	0.167	0.043	0.210	0.098	0.019	0.009	0.0029	0.129
80 10 10 (Monte Carlo)	0.6116 (1.43%)	0.0842 (1.72%)	0.0324 (1.66%)	0.1166 (1.31%)	0.0969 (1.77%)	0.0246 (1.66%)	0.0046 (1.98%)	0.0019 (1.90%)	0.1280 (1.36%)
(Numerical)	0.615	0.085	0.033	0.118	0.097	0.025	0.005	0.0019	0.128

[a] Average predicted relative standard deviation for all the total intensities = 1.47%. Average most probable relative error for all the total intensities = 0.95%.
[b] Predicted relative standard deviations given in parentheses.
[c] Numerical results taken from Ref. [6].

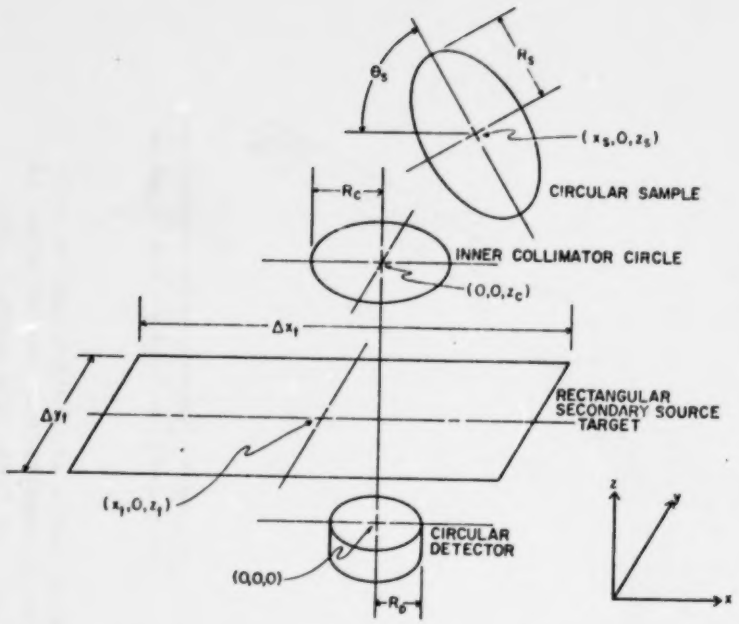

Figure 16. Schematic diagram of the arrangement and nomenclative of the rectangular secondary source target and circular sample in relation to the circular detector and collimator for the Monte Carlo simulation of a secondary fluorescer EDXRF system.

A typical experimental secondary source intensity distribution is shown in Figure 17. Typical Monte Carlo results as compared to experimental data are shown in Figures 18, 19, and 20. It is clear from these results that the method is quite accurate.

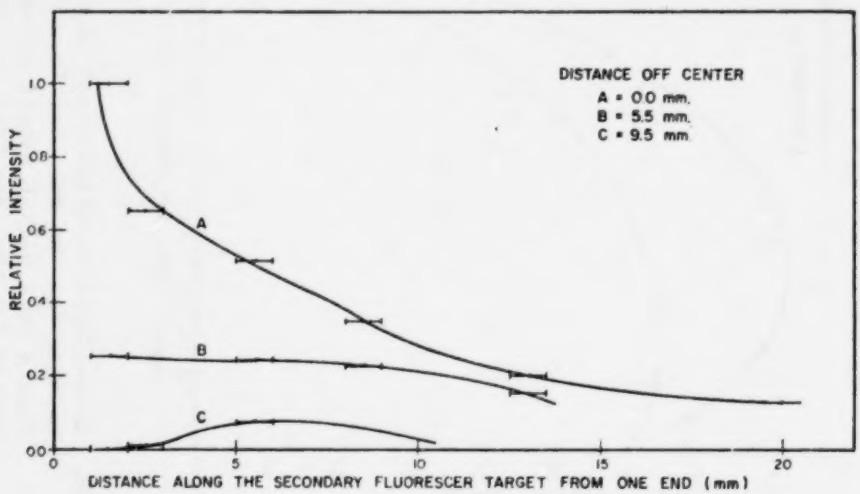

Figure 17. A typical experimental secondary source intensity distribution.

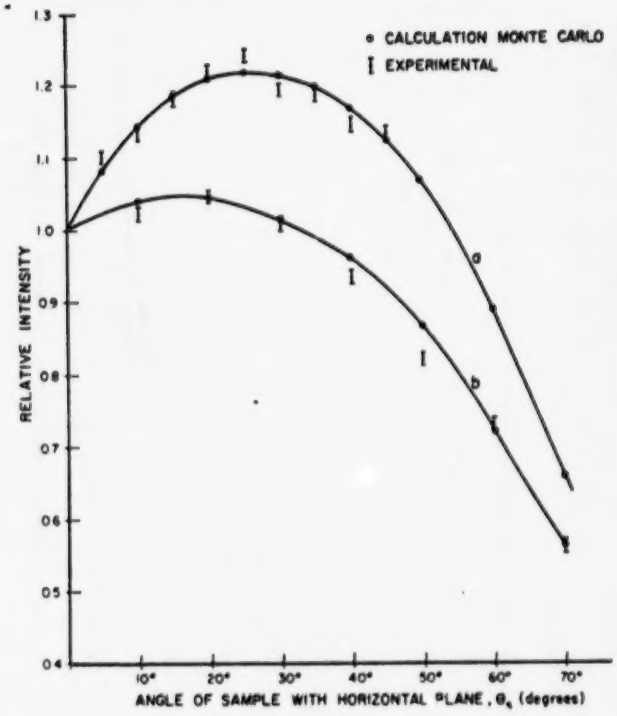

Figure 18. Monte Carlo simulation and experimental results for the relative intensities from a pure nickel sample at various angles for the Case 1(a) and Case 2(b) system parameters given in Table I.

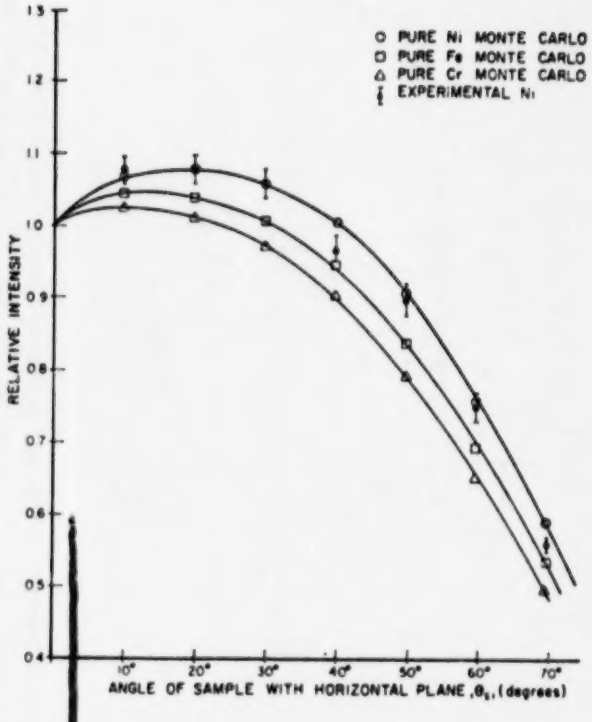
PURE Ni MONTE CARLO
PURE Fe MONTE CARLO
PURE Cr MONTE CARLO
EXPERIMENTAL Ni
RELATIVE INTENSITY
ANGLE OF SAMPLE WITH HORIZONTAL PLANE, θs (degrees)

Figure 19. Monte Carlo simulation and experimental results for the relative intensities from pure nickel, pure iron, and pure chromium samples at various angles for the Case 3 system parameters given in Table I.

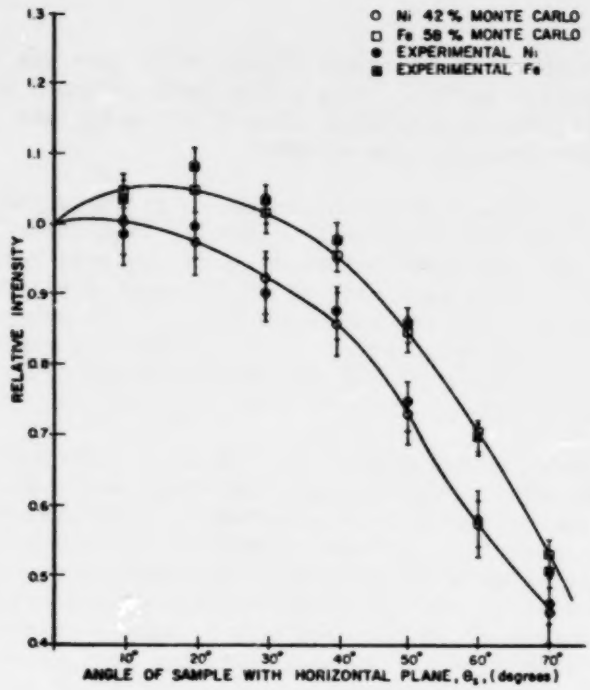

Figure 20. Monte Carlo simulation and experimental results for the relative intensities from a 42 percent nickel - 58 percent iron binary sample at various angles for the Case 3 system parameters given in Table I.

The primary anticipated use of the Monte Carlo simulation is in the calibration of EDXRF analyzer systems. Although the calibration could be performed in a number of ways, the primary use of the Monte Carlo simulation would almost always be in providing "bench mark" responses for samples of known composition and other pertinent properties. If one adopts the usual experimental technique of obtaining responses as the response from the sample of interest divided by the response from a pure sample of the appropriate element, then Monte Carlo simulations could be used to provide accurate "synthetic" standards of this type. These could be used instead of actual standards with experimental responses for preparing empirical calibration relationships. The advantages of this procedure include: (1) being able to obtain better accuracy since alternate elemental analyses are not required, (2) eliminating the expense and time-consuming process of preparing actual standards and obtaining experimental responses, and (3) being able to select the range of standard compositions and other properties pertinent to the analyses to be performed without physical limitations.

Another second order use of the Monte Carlo simulation is in the optimum geometrical design of secondary fluorescer EDXRF analyzer systems. In order to use the Monte Carlo simulation in this way it is desirable to modify it to include the scatter of the exciting radiation (Compton and Rayleigh) so that

one will be able to evaluate what is usually taken as either the signal-to-noise or signal-to-background ratios. This modification should be relatively easy to make in principle, but in practice some of the pertinent interaction cross sections may be inaccurate or unavailable.

This brings up the additional point of interest to the authors which is to provide predictions of complete spectral responses from EDXRF analyzer systems so that more of the available information can be used for analysis purposes. While it is true that much more elemental analysis information is contained in the characteristic X-ray responses than in the scattered response, nevertheless additional useful information is available from this latter source. The approach of utilizing all of the available spectral information is presently being investigated.

While the present Monte Carlo simulations are very efficient since essentially complete variance reduction techniques have been employed, the calculations are still quite time consuming and expensive. Therefore, the Monte Carlo simulation will probably not often be used in routine calculation such as in the small computers association with EDXRF analyzer systems or even in off-line computations on large computers for individual sample data processing. There is a need for the development of simple approximate models to replace the Monte Carlo simulation for routine use. It appears that one very promising approach is to use either the average angle approach (6,7) directly or a suitable modification of it. This approach essentially consists of obtaining the average entrance and exit angles for a given EDXRF analyzer system by Monte Carlo simulation. Then with these average angles one may use either the explicit analytical equations originally derived by Sherman (20,21) for thick homogeneous samples or a suitable equation like that derived by Dzubay and Nelson (24) for other types of samples to simulate sample responses. One modification of this would be to use two or more different radiation paths at fixed entrance and exit angles within the range of these angles that exist in the EDXRF analyzer system. This approximation is presently under study.

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APPENDIX

List of Reports, Theses, and Publications Either Entirely or Partially Supported by this Grant

Reports

Gardner, R. P., F. Arinc, E. Efird, L. Wielopolski, A. R. Hawthorne, and K. Verghese. Mathematical Techniques for X-Ray Analyzers, Technical Progress Report, U.S.E.P.A. Grant No. R-802759, for period May 15, 1974, to May 14, 1975.

Gardner, R. P., F. Arinc, A. R. Hawthorne, L. Wielopolski, G. R. Beam, and K. Verghese. Mathematical Techniques for X-Ray Analyzers, Technical Progress Report, U.S.E.P.A. Grant No. R-802759, for period May 15, 1975, to May 14, 1976.

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Arinc, S. Faruk. Mathematical Methods for Energy Dispersive X-Ray Fluorescence Analysis. Ph.D. Thesis, North Carolina State University, Raleigh, North Carolina, 1976. 164 pp.

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Hawthorne, Alan R. Mathematical Models for Interelement and Matrix Effects in X-Ray Fluorescence Analysis. Ph.D. Thesis, North Carolina State University, Raleigh, North Carolina, 1977. 185 pp.

Wielopolski, Lucian. Utilization of Si(Li) Detector Response Function and Pile-Up Model in the Analysis of X-Ray Spectra. Ph.D. Thesis, North Carolina State University, Raleigh, North Carolina, 1979. 85 pp.

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Arinc, F., R. P. Gardner, L. Wielopolski, and A. R. Stiles. Application of the Least-Squares Method to the Analysis of XRF Spectral Intensities from Atmospheric Particulates Collected on Filters. Advances in X-Ray Analysis, 19:367-380, 1976.

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